Characterization of Air Manganese Exposure Estimates for Residents in Two Ohio Towns

Michelle Colledge[a], Jaime Wagner[b], Vihra Gocheva[c], CherylBeseler[d], Harry Roels[e], Danelle Lobdell[f], Rosemarie Bowler[c]

[a]ATSDR, Region 5, 77 W. Jackson Blvd., MS ATSD-4J Chicago, IL 60604 USA

[b]U.S. EPA, Region 5, 77 W. Jackson Blvd., AR 18-J, Chicago, IL 60604 USA

[c]San Francisco State University, Department of Psychology, 1600 Holloway Ave. San Francisco, CA USA

[d] Colorado State University, 1879 Campus Delivery, Fort Collins, CO USA

[e]Louvain Centre for Toxicology and Applied Pharmacology, Université catholique de Louvain, Avenue Mounier 53.02, 1200 Brussels, Belgium

[f] U.S. EPA, National Health and Environmental Effects Research Laboratory, MD 58A Research Triangle Park, NC 27711 USA

Corresponding Author:

Michelle Colledge

ATSDR-Region 5

77 W. Jackson Blvd, Room 413, MS-ATSD-4J

Chicago, IL 60604

Ph: +312-886-1462

Fax: +312-886-6066

mcolledge@cdc.gov

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Abbreviations and definitions:

Air-Mn – Air Manganese; cMRL – chronic Minimal Risk Level; Mn – Manganese; Mn – Blood Manganese; MnH – Hair Manganese; TSP – Total Suspended Particulate;

Abstract

Background: Few available studies evaluate long-term health outcomes from inhalational manganese (Mn) exposure in residential populations, due in part to challenges in measuring individual study subject exposures.

Objectives: The objective of this study was to derive receptor-specific air manganese (air-Mn) inhalation exposures for two Ohio communities with very different emission and concentration profiles with source-emission data gaps.

Methods: U.S. EPA's AERMOD dispersion model and air measurement data were used to estimate concentrations for resident-specific receptor sites in two study communities. Detailed emissions data from a Mn smelting operation were used for modeling air-Mn in the first community. Since no emissions data were available in the second community near a Mn-ore processing and storage facility, the AERMOD model was run using a unit emission factor and the results calibrated with measured data from a local air quality monitoring station. The ratio of modeled to monitored air concentrations were then used to adjust the modeled results at the receptor sites.

Results: Modeled estimates of annual mean outdoor air-Mn exposures from particulates at residential locations were as high as 1.93 $\mu g/m^3$. Estimated air concentrations were consistent with the range of measured outdoor air-Mn in the communities where air modeling was conducted.

Conclusions: Data from local air monitoring stations can provide the means to calibrate models used in estimating long-term exposure to Mn. Furthermore, this combination of modeling and

ambient air sampling can be used to derive these estimates even in the absence of source emission data.

Introduction

Only a few inhalation exposure studies have evaluated non-occupational, stationary source-based environmental exposures to manganese (Mn). Although Mn inhalation exposure in the general population is much lower than in the occupational setting, these studies also identified subtle neurological deficits in residential populations chronically exposed to low air-Mn levels (Baldwin et al., 1999; Beuter et al., 1999; Bowler et al., 1999; Lucchini et al., 2012; Menezes-Filho et al., 2011; Mergler et al., 1999; Riojas-Rodriguez, et al. 2010, Rodriquez-Agudelo, 2006).

The first account of Parkinsonian symptoms linked to inhalation exposure of Mn was documented by Couper in 1837. Since then, the epidemiologic literature has established that adverse neurological and neuropsychological health effects are associated with chronic human exposure to excessive airborne manganese (air-Mn) via inhalation. Occupational studies have described motor impairment (e.g., psychomotor speed, reaction time, hand-eye coordination, postural sway), cognitive deficits (e.g. verbal IQ, working memory), mood perturbations (e.g., depression, anxiety), and depressed olfaction in workers (microsmia, anosmia) with average Mn exposures as low as 32 $\mu g/m^3$, with increasing severity for higher exposures (ATSDR, 2008; Blond and Netterström, 2007; Bowler et al., 2006, 2007, 2011; Chia, 1995; Iregren, 1990; Lucchini et al. 1995; 1999; Mergler et al., 1994, Roels et al., 1985, 1987, 1992, 1999, 2012).

Environmental air-Mn concentrations in the United States vary significantly with location and proximity to emissions sources. Based on national air monitoring networks, the average

background air-Mn concentration in urban areas is approximately 0.05 µg/m^3 (U.S.EPA, 2012a). U.S.EPA (1984) reported that rural Air-Mn from 1965-1982 was approximately 6.25 times lower than urban air-Mn. Air-Mn in areas with Fe/Si-Mn alloy smelters or other operations using Mn-containing products can be several orders of magnitude higher than what has been reported in rural and urban environments (ATSDR 2008; 2009; 2010).

Two communities in Northeast Ohio were identified with elevated measured concentrations of ambient air-Mn, one of which has the highest concentrations of measured air-Mn reported to the United States Environmental Protection Agency (U.S.EPA) Air Quality System (AQS) database (U.S.EPA, 2012a). Air-Mn in one community (Marietta) is predominantly released from a large ferro-alloy smelting plant (Eramet, Inc.) while in the other community (East Liverpool) it is released during the offloading, grinding (for resizing), packaging, and storage of Mn-containing ore products at a metals storage and packaging facility (S.H. Bell Company). East Liverpool is approximately 200 km NNE of Marietta, along the Ohio River.

Residents from each community were recruited to participate in a study examining neurological and neuropsychological impacts from chronic exposures to low levels of manganese. In support of this epidemiologic study, modeled estimates of outdoor air-Mn concentrations were derived as surrogates of exposure for residents identified as study participants in the two communities. Highly detailed emissions inventories obtained from the ferro-alloy smelting plant were used to conduct dispersion modeling and estimate long-term Mn inhalation exposure for each study participant in the Marietta community. Because emissions data were not available for the packaging and storage facility, dispersion modeling calibrated with measured data was used to estimate air-Mn exposures for each study participant in the East Liverpool community. Both communities had over 10 years of

environmental total suspended particulate (TSP) sampling data generated between 1999 and 2011 that were analyzed for a number of heavy metals, including Mn. Only years where data met 75% completeness were used for statistical analyses.

The objective of this study was to estimate inhalation exposures to outdoor air-Mn for residents of two Ohio communities with different emission and source concentration profiles.

Materials and Methods

Stationary monitoring and fingerprinting of ambient TSP air-Mn:

TSP samples have been continuously collected and analyzed by the Ohio Environmental Protection Agency (Ohio EPA) since 2000 in Marietta and 2003 in East Liverpool (See Table 1), though 10 months of continuous data were also collected in 2000 in East Liverpool. Stationary high volume ("HiVol") monitors used in these communities pull ambient air through an orifice at the top of the monitor at a volume rate of 1.13 m^3/min and particulate is deposited on a 203 x 254-mm glass fiber filter according to U.S.EPA Compendium Method IO 2.1 (U.S.EPA, 1999a). The concentration of TSP was reported as mass of particulate matter collected per cubic meter of air sampled ($\mu g/m^3$) at sea level pressure (1 atm) and a temperature of 25°C (ATSDR, 2007). Sample filters were analyzed for metals using inductively coupled plasma/mass spectrometry (ICP/MS) according to the U.S.EPA Compendium Method IO 3.5 (U.S.EPA, 1999b).

At both sites, 24-hour TSP filter samples have been collected in community air monitoring stations every 6 days. These 24-hour samples are composited and analyzed to create a monthly average (Ohio EPA 2012a,b). Because composite sample concentrations of Mn were elevated, in 2005, Ohio EPA began analyzing every filter from the East Liverpool Water Plant air monitoring station in individual 24-hour samples (discrete) as well as monthly

composite samples to yield more information about the magnitude of manganese levels in community outdoor air (Ohio EPA, 2012b). Thus, data at this location were evaluated as both 24-hour and monthly averaged composite samples (ATSDR, 2010). Figures 1 and 2 present the locations of air monitoring sites relative to the Mn source facilities.

To understand the sources and toxicological implications of exposure to air-Mn, the U.S.EPA National Enforcement Investigations Center (NEIC) Laboratory analyzed Mn collected on existing filters at stationary sampling locations in Marietta and East Liverpool. These analyses were carried out to yield information about how metals on the filters at various locations are related and how they compare to source samples, to evaluate size distribution and morphology of collected particulate, and determine the elemental abundance and chemical form of metals on the filters. For the purposes of these analyses, air filters were evaluated by using LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometry), SEM (scanning electron microscopy), and XRD (X-ray diffractometry) techniques (U.S.EPA 2010b, U.S.EPA, 2010c).

Size fractions of particulates in East Liverpool air samples were also determined from collocated air monitors at the Water Plant operated by Ohio EPA and U.S.EPA. The monitors collected 24-hour TSP, PM_{10}, and $PM_{2.5}$ samples for three months in summer of 2011.

Identification of Modeling Receptor Points:

Receptor points consisted of monitoring stations and the residential location of people recruited as part of two population studies that examined the potential health effects of air-Mn exposure in adult residents of Marietta, Ohio (n=100) and East Liverpool, Ohio (n=86). Figures 1 and 2 show the generalized location of the study subjects in each town relative to the air

monitoring stations and the Mn emissions source facilities. Study participants for each community were identified based on the likelihood of elevated exposures based on historically measured and previously modeled data. The study participants were obtained by random recruitment in these areas and application of eligibility criteria as described for Marietta by Bowler, et al., (2012). Study subjects underwent a number of neuropsychological tests and submitted toenail, hair, and blood samples for analysis. Data collection in these communities took place in 2009 and 2011 for Marietta and East Liverpool, respectively.

Model methodology:

AERMOD is U.S. EPA's preferred dispersion model for short-range (less than 50 kilometers) modeling analyses. The AERMOD modeling system consists of two preprocessors and a dispersion model (Cimorelli et al., 2005):

- A meteorological preprocessor (AERMET) uses meteorological data and surface characteristics to develop planetary boundary layer parameters to create profiles of wind, turbulence, and temperature;
- A terrain preprocessor (AERMAP) uses gridded terrain data to determine the influence of elevation on the modeling domain, which allows AERMOD to calculate concentrations in either flat or complex terrain;
- A steady-state plume model (AERMOD) designed to estimate impacts in urban or rural areas, in flat or complex terrain, for surface or elevated releases from multiple sources and multiple source types.

Land use/land cover data and one arc-second (approximately 30 m) National Elevation Dataset for the study areas were acquired from the United States Geological Survey Seamless

Server (USGS, 2012). Weather data were acquired from the nearest National Weather Service (NWS) stations for the two communities which provided current hourly surface observations and upper air sounding data (NCDC, 2012).

Air dispersion modeling for Marietta:

AERMOD was used to predict average air-Mn concentrations near each modeled receptor (home of each resident study volunteer). The inputs to the model included:

1) the nearest and most representative NWS surface station located at the Mid-Ohio Valley Regional Airport in Parkersburg, WV, approximately 8 km east-southeast of the facility. Five consecutive years of meteorological data (1991-1995) were processed through AERMET;

2) the nearest NWS upper air station with data for the same 5-year period is at the Wright-Patterson Air Force Base in Dayton, OH, which is approximately 322 km west-northwest of the facility;

3) the Mn source facility (Eramet, Inc.) provided U.S.EPA Region 5 with particulate matter emissions data for the facility's various processes, along with percentages of manganese for each process. These values were used to calculate Mn emissions for all reported processes, which onsite totaled 255 tons for year 2001. All non-stack sources were modeled as volume sources (U.S.EPA, 2010a).

Air dispersion modeling for East Liverpool:

No emissions data were available for the metals packaging and storage facility in East Liverpool. To estimate residential air-Mn inhalation exposure for each study subject, AERMOD was used to determine exposure ratios of each residence to a reference point. The Water Plant

monitor was chosen to be the reference point because it is the closest of three area air monitoring stations to the Mn emissions source. The Water Plant monitor station also has the longest history of discrete 24-hour analysis on filters (since 2005; discrete analyses at the other sites began in 2011); prior to that time, only monthly composite data were reported.

The nearest and most representative meteorological station is located at the Pittsburgh International Airport in Pittsburgh, PA, which is approximately 40 km southeast of the facility. National Climatic Data Center (NCDC) 1-minute surface data, NWS hourly surface data, and NWS upper air data are all available for this station. Five consecutive years of data (2006-2010) were processed through AERMET (U.S.EPA, 2012b).

To assist in calculating individual exposure estimates, AERMOD was used to calculate 5-year average air concentrations from a unit emission rate of 1 gram per second (g/s) over the 186,155 m^2 surface area (42 acres) of the facility. Dispersion modeling is linear, thus choosing a scalable unit emission rate, like 1 g/s, facilitates calculating estimated outdoor concentrations from many on site sources without re-running the model for each source. This procedure is recommended for dispersion modeling (U.S.EPA, 2005).

The unit emission rate was used for modeling purposes to calculate ratio relationships between estimated air-Mn concentrations at receptor points. Using this approach, the relationships of the modeled concentrations to each other and to a known reference point (in the form of estimated exposure ratios) can be used to calculate estimated air-Mn exposures. In this instance, the known reference point was historical data recorded at the Water Plant outdoor air monitoring station. AERMOD model outputs for estimated outdoor air-Mn were scaled to actual measurements at the Water Plant monitoring station, yielding a relative fraction of air-Mn measured at the Water Plant for all receptor points. As with Marietta,

topography, location, and meteorology were required inputs in order to run the model. For calculating exposure estimates of East Liverpool residents, annual average air-Mn measurements were used to derive estimated exposures from air-Mn ratios calculated using AERMOD ambient concentration outputs. The method for calculating the estimated exposure of each receptor point was defined as:

$$\mathrm{R(air-Mn)} = \frac{\mathrm{AR}(\mu g/m^3)}{\mathrm{AWP}(\mu g/m^3)} * \mathrm{C}(\mu g/m^3)$$

Where R(air-Mn) is the estimated exposure of Mn for each receptor; AR is the receptor-specific AERMOD estimate of air-Mn derived from the unit emission rate of 1 g/s; AWP is the AERMOD estimate of air-Mn derived from the unit emission rate at the Water Plant station; and C is the annual average air-Mn concentration measured at the Water Plant station. A comparison of the models run for Marietta and East Liverpool is displayed in Table 2.

Statistics

Raw data from area air monitors were obtained in Microsoft Excel files. Descriptive statistics were generated to qualitatively compare measured and modeled data for each town and exposure ratios and estimates were calculated for East Liverpool using Microsoft Excel 2007.

Results

Stationary sampling data of TSP air-Mn

The statistical summary for the five Marietta air monitor locations (Table 3) shows that over the 12-year sampling period, air-Mn TSP air samples frequently exceeded the background

values typical of ambient air-Mn in urban areas (U.S.EPA, 2012a). Across the five sampling sites, the arithmetic mean (AM) of the monthly composite air-Mn concentrations ranged from 0.10 $\mu g/m^3$ to 0.39 $\mu g/m^3$. For comparison, the manganese concentrations for eight 24-hour samples collected on the facility property averaged (AM) 1.13 $\mu g/m^3$ and ranged from 0.46 to 1.90 $\mu g/m^3$ (Eveready, Table 3). In East Liverpool, the majority of monthly air-Mn concentrations also exceeded the national background concentration. Across the three sampling sites the AM ranged from 0.20 to 1.55 $\mu g/m^3$ (Table 4). Air-Mn concentrations for 24-hour samples ranged from 0.02 to 25.0 $\mu g/m^3$ and averaged 1.71 (AM) and 0.68 $\mu g/m^3$ geometric mean (GM) (Table 4). TSP air-Mn in both communities exceeded the chronic ATSDR Minimal Risk Level (0.04 $\mu g/m^3$) and the U.S.EPA reference concentration (0.05 $\mu g/m^3$) for at least one community monitoring site in nearly every reported measurement date during the 12 year sampling period.

NEIC's fingerprinting analysis consisted of evaluating 341 glass fiber HiVol 24-hour sample filters from the five monitoring sites within the Marietta area (U.S.EPA, 2010b). The SEM analyses indicated that ambient air-Mn particulate on the filters was predominately spherical (77%) and that the chemical form of Mn was generally Mn-oxide. The analysis also determined that 83% of TSP-Mn was respirable with Mn particles having an aerodynamic diameter (d_{ae}) ≤ 10 µm (PM_{10}) and 21% with a d_{ae} ≤ 2.5 µm ($PM_{2.5}$). More than half of the Mn particles were smaller than 5 µm. The greater prevalence of fine Mn particles in Marietta is consistent with the fine metal dusts released from high-heat processes, such as smelting (U.S.EPA, 1996).

In 2011, collocated air monitors were sited and operated by Ohio EPA and U.S.EPA at the East Liverpool Water Plant location for collection of 24-hour TSP, PM_{10}, and $PM_{2.5}$ samples. From these samples, it was determined that TSP from East Liverpool has a greater percentage

of non-respirable Mn particles compared to Marietta TSP. In East Liverpool, 35% of TSP consisted of respirable PM_{10} Mn whereas only 3.7% of the TSP Mn was $PM_{2.5}$ Mn. This is consistent with SEM fingerprinting analysis conducted by NEIC on a limited number of East Liverpool TSP filters indicating Mn particles in East Liverpool have a d_{ae} range of 4.4 to 24.3 µm (U.S.EPA, 2010c). A generally larger Mn particle fraction was expected given that emission points at the source facility in East Liverpool are general offloading, storage, and sizing/grinding operations. Estimated annual concentrations of PM_{10} Mn and $PM_{2.5}$ Mn were generated using the ratios determined from fingerprinting and monitoring, and descriptive statistics were generated to compare inhalation exposures in the communities.

Exposure Estimates:

Annual average (AM) inhalation exposure estimates were calculated for each receptor point in East Liverpool using sufficiently complete discrete 24-hour and adjusted monthly averaged data collected between 2000 and 2011 (2000; 2003-2011). Data from the seven years of sampling (2005-2011) where both discrete and composite data were available indicated that annual averaging of air-Mn derived from composite data generally resulted in a 16.4% underestimation of the average compared to annual averages derived from discrete data. Thus, for the years with composite data only (prior to 2004), the annual averages were adjusted up 16.4% based on discrete data to correct for the differences observed between averaging with composite and discrete observations (Table 5).

Table 6 shows annual average exposure estimates of TSP air-Mn in Marietta and East Liverpool derived solely from AERMOD in Marietta and from AERMOD and measured data in East Liverpool. In Marietta, the modeled exposure estimates ranged from 0.04 µg/m^3 at the lowest receptor point to 0.96 µg/m^3 at the highest receptor point, with an average annual

exposure for all receptor points of 0.18 μg/m^3 (AM) and 0.16 μg/m^3 (GM). Across the sampling period in East Liverpool, the modeled exposure estimates of air-Mn TSP ranged from 0.004 μg/m^3 at the lowest exposed receptor point to 1.93 μg/m^3 at the highest exposed receptor point, with an overall average annual exposure for all receptor points of 0.27 μg/m^3 (AM) and 0.11 μg/m^3 (GM). The statistical distribution of modeled TSP air-Mn were within the range of measured air-Mn concentrations across all monitors located in each community (Table 6), which provides internal consistency for the calculation approach used in the present study.

Descriptive statistics were calculated for the fraction of modeled air-Mn TSP estimated to be PM_{10} and $PM_{2.5}$ using scaling factors derived from the fingerprinting analyses for the Marietta study and collocated measurements for the East Liverpool study. Table 7 presents the statistical distribution of these estimates in Marietta (PM_{10}: 0.15 μg/m^3 (AM), range 0.03 to 0.80 μg/m^3; $PM_{2.5}$: 0.04 μg/m^3 (AM), range 0.008 to 0.20 μg/m^3) and East Liverpool (PM_{10}: 0.04 μg/m^3 (AM), range 0.002 to 0.68 μg/m^3; $PM_{2.5}$: 0.01 μg/m^3 (AM), range 0.0002 to 0.07 μg/m^3), which indicate that even though the TSP air-Mn levels in East Liverpool were at times over 100-fold higher than in Marietta, the Marietta residents have a higher exposure to respirable Mn particulate. The implications of this finding will be explored in subsequent epidemiologic studies in these towns.

Discussion

Public health concern regarding air-Mn exposures has been acknowledged since the 1970s and probably earlier (Joselow et al., 1978). Government regulation for anthropogenic sources stemming from these health concerns and epidemiologic research on long-term low-level inhalation exposure to Mn in ambient air began in the United States with the publication

of a U.S.EPA reference concentration (RfC) value of 0.050 µg/m³ in 1993 (U.S.EPA, 2012c). RfC supporting documents initially focused on the potential risk of Mn emissions from mobile sources from the incomplete combustion of the gasoline additive methyl-cyclopentadienyl manganese tricarbonyl (MMT) (Davis, 1998). However, subsequent studies have suggested that industrial sources of air-Mn may have greater impacts to ambient air than motor vehicle exhaust from the combustion of gasoline containing MMT (ATSDR, 2008).

Comparison to TSP air-Mn studies

The mean air-Mn concentrations measured in Marietta and East Liverpool are comparable to those reported in other studies documenting adverse health effects in communities. The range of composite TSP air-Mn averages across all sampling sites sampled between 2000 and 2011 was 0.10 µg/m^3 to 0.39 µg/m^3 in Marietta and 0.20 to 1.55 µg/m^3 in East Liverpool. A community study in Quebec that identified neuromotor and neuropsychological deficits and mood changes reported an average TSP air-Mn concentration of 0.022 µg/m^3 with a range of 0.009-0.035 µg/m^3 (Baldwin et al., 1999; Beuter et al., 1999; Bowler et al., 1999; Mergler et al., 1999). In this study, four days of ambient air sampling were available to assess inhalation exposures.

Comparison to PM_{10} air-Mn studies

Estimated PM_{10} air-Mn exposures derived from measured and modeled data for Marietta had a mean air-Mn concentration of 0.15 µg/m^3 and East Liverpool had mean air-Mn concentration of 0.04 µg/m^3. Rodriguez-Agudelo et al. (2006) reported a statistically significant association between air-Mn concentrations and altered neuromotor function in residents living

at various distances from Mn mining operations where limited samples collected at 28 residences in 8 communities had a mean PM_{10} air-Mn concentration of 0.42 µg/m³. Personal exposure estimates were not available to conduct regression analyses of motor test results; however, residents living nearest air monitors with elevated relative exposures were identified as having a higher risk of motor dysfunction. Riojas-Rodriguez et al. (2010) reported a decline in cognitive function in female children with increasing Mn concentrations in hair (MnH) in this same community. Lucchini et al. (2012) reported deficits in olfactory and motor function in adolescents exposed to elevated levels of PM_{10} air-Mn from historical ferro-Mn alloy operations with an average PM_{10} air-Mn concentration of 0.05 µg/m^3. The study did not note associations between air-Mn levels and health outcomes. However, multiple confounders complicate the interpretation of these results, including a limited personal air sampling duration of 24 hours.

Comparison to $PM_{2.5}$ air-Mn studies

Similar findings correlating elevated MnH with a reduction in cognitive function in mothers and their children in Brazil who were exposed to ferro-Mn alloy emissions (Menezes-Filho et al., 2011), where $PM_{2.5}$ air-Mn averaged 0.15 µg/m^3 (Menezes-Filho et al., 2009). Estimated $PM_{2.5}$ air-Mn based on modeled and measured data averaged 0.04 and 0.01 µg/m^3 in Marietta and East Liverpool, respectively. Haynes et al. (2012) conducted a study in Marietta to evaluate the relationship between $PM_{2.5}$ air-Mn and blood manganese (MnB) and MnH levels in 38 children but also collected limited (4 days) personal and stationary $PM_{2.5}$ air-Mn samples. The GM concentration of $PM_{2.5}$ air-Mn collected during the study was reported to be 0.008 µg/m^3. No correlation was identified between personal and stationary air-Mn sampling and

MnB or MnH levels, however the sampling duration was limited to four days over a two-year period and more than half of the study subjects were located east of the source facility while the general wind direction in Marietta is out of the southwest (resultant wind direction is 227 degrees).

Marietta and East Liverpool have a rich database of measurements from which to derive potential historical exposure information. Furthermore, U.S.EPA data confirms that the communities of Marietta and East Liverpool, OH have some of the highest measurements of air-Mn in the United States (U.S.EPA, 2012a). Thus, further evaluation of health outcomes and biomarker associations with air-Mn in these communities is warranted.

Health Outcomes and Modeled Data

Haynes et al. (2010) conducted a pilot study examining the relationship between modeled outdoor air manganese and concentrations of biomarker concentrations of Mn in hair (MnH) and blood (MnB) in the community living near Eramet, Inc. in Marietta. Kim et al. (2011) and Bowler et al. (2012) measured a number of neurological and neuropsychological health outcomes in the same exposed community as Haynes et al. (2010) but also included an analysis of a control population in Mount Vernon, Ohio. The emissions data utilized in the Kim et al. (2011) and Bowler et al. (2012) studies were provided directly to U.S.EPA by the facility and were highly detailed and process-specific. The AERMOD estimated outdoor TSP air-Mn concentrations for those studies ranged 0.04 to 0.96 $\mu g/m^3$ with a mean of 0.18 $\mu g/m^3$. In the same community, the Haynes et al. (2010) study estimated a range of TSP air-Mn of 0.01 to 18.13 $\mu g/m^3$ and mean of 0.13 $\mu g/m^3$ using the AERMOD model, but used Toxic Release Inventory (TRI) Data as the source term. Since 2000, Ohio EPA has monitored Marietta Air-Mn

concentrations similar to those modeled and reported in Kim et al. (2011) and Bowler et al. (2012). The highest annual average detected at any monitoring station in Marietta (0.35 $\mu g/m^3$) was near the Eramet property fenceline (ATSDR, 2007; ATSDR 2009).

The differences observed in these studies of modeled air-Mn concentrations and with monitored data highlights the importance of using site-specific emissions data to estimate exposures, and in the absence of such (e.g., relying solely on TRI data) how critical measured data can be to validate air modeling efforts.

Summary

In East Liverpool, over 10 years of air monitoring data were available to assess Mn inhalation exposure, but at only 3 monitoring sites in the community. AERMOD was used to estimate air-Mn concentration and determine corresponding relationships between each residential receptor point and the Water Plant reference point. Using exposure ratios, annual average concentrations at the Water Plant site were used to calculate annual estimated exposures for each study participant.

A number of unquantified parameters exist that may influence the extent to which outdoor air-Mn relates to true exposures. The results of this analysis do not include parameters such as activity patterns, deposition, and residential and resuspended Mn from ambient sources into account; however, ratios derived from modeled long-term average concentrations can be used for a surrogate of inhalation exposure. Potential uncertainties with the meteorological data used in Marietta may exist as well. The hourly surface data used in the Marietta modeling is from 1991-1995, which was chosen at the time due to concerns about the collection and reporting of newer data. While these concerns have now been addressed by the

availability of 1-minute surface data, these data were not readily available at the time of the Marietta modeling. The upper air data used in Marietta was from a station 322 km away. Upper air data stations are not as prevalent as surface stations because upper air data are regionally representative (as opposed to locally representative surface data). Additionally, complex terrain in the vicinity of both Marietta and East Liverpool can affect the predicted concentrations. While terrain elevations were taken into account in the modeling, higher data resolution could have affect estimated concentrations. The highly variable loading, grinding, and packaging schedule, along with constantly changing ore sizes and sources at the East Liverpool facility, makes emissions calculations impractical. Due to the lack of facility-specific information in East Liverpool, the source parameters and emission rates for the facility were based entirely on generic assumptions. For example, the unit emission rate of 1 g/s from the entire 42 acre facility was assumed to be emitted continuously over the modeled 5-year period. Assuming a continuous emission rate is standard modeling procedure in instances where there is no basis for allocating variable emissions. Since site-specific processes at the facility were not taken into account and a unit emission rate was used, the facility's ambient impact on annual average air-Mn concentrations may be over or under-predicted.

In spite of missing emissions data in East Liverpool, this paper outlines how individual exposure estimates were calculated for study participants recruited in Marietta and East Liverpool using air dispersion modeling. Estimated exposures are validated by measured air-Mn concentrations reported since 2000 in both communities. From this information, analyses of neurological and neuropsychological health outcome data can be conducted using study-subject specific exposure estimates. This approach is useful for other epidemiologic studies

where the researchers wish to evaluate health outcomes as they relate to environmental exposures in the absence of personal sampling data.

Conclusions

Exposure estimates can be derived directly from modeling facility emissions or can be extrapolated from other methods when emissions data are unavailable. In instances where limited outdoor monitoring data are available, modeling using generic emission rates can yield important information about the relative magnitude of exposure within a geographic area. Annual average manganese exposures were calculated for the residential receptor points of each study participant In Marietta and East Liverpool.

Using measured and modeled data, concentrations of respirable manganese for study participants were calculated in the two Ohio study populations. This method for estimating personal exposures can prove useful in future studies to assess the relationship between adverse health outcomes and personal exposures to environmental pollutants, where the collection of such data are unfeasible and limited air monitoring data are available.

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Figure 1. Location of Study Communities

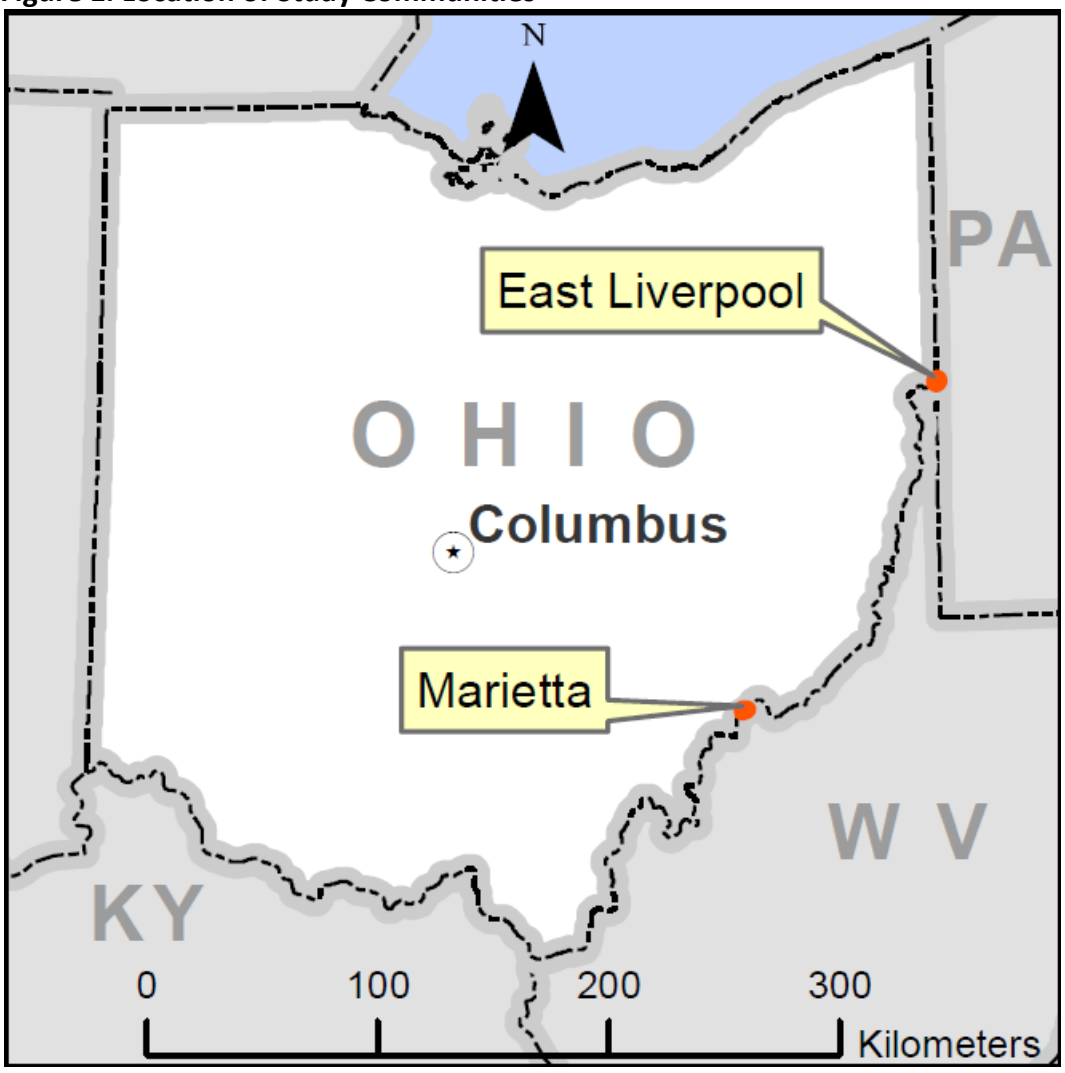

Figure 2. Marietta Map of Air Monitor and Study Subject Locations

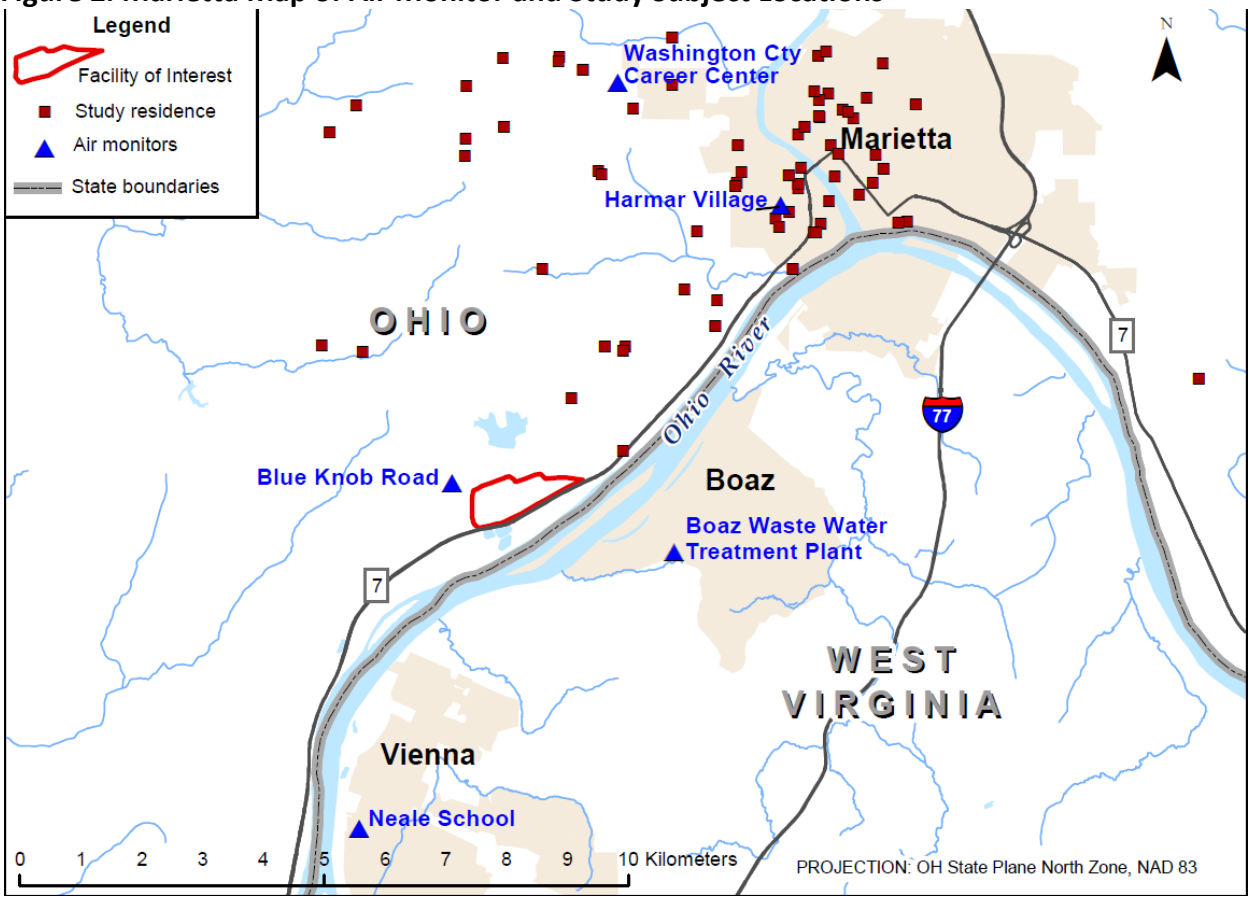

Figure 3. East Liverpool Map of Air Monitor and Study Subject Locations

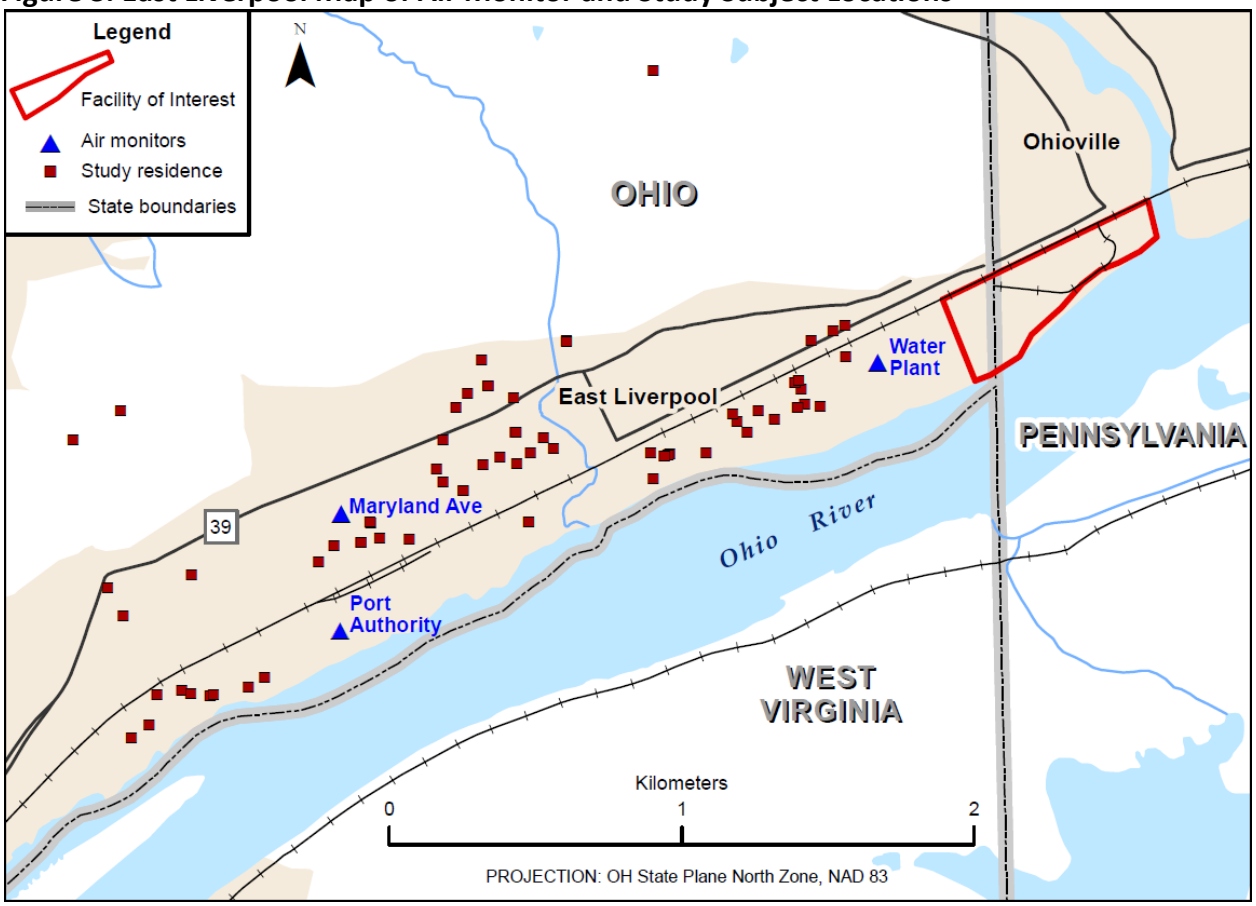

Table 1. Historical sampling in Marietta and East Liverpool

City	Site	Sampling Range	Sampling Frequency	Particulate Fraction	Mn Range of Detection (ug/m3)
Marietta, OH	Washington County Career Center	2000-2012	1 in 6 days; averaged monthly	TSP	0.01-1.50
Marietta, OH	Blue Knob Road	2004-2006; 2009	1 in 6 days; averaged monthly	TSP	0.05-1.30
Marietta, OH	Eveready	2006	1 in 6 days; averaged monthly	TSP	0.46-1.90
Marietta, OH	Neale Elementary, Harmar Village, Boaz	2007-2008	1 in 6 days; averaged monthly	TSP	0.02-0.38
East Liverpool	Water Plant	1999-2001; 2003-2012	1 in 6 days; averaged monthly	TSP	0.10-6.80
East Liverpool	Water Plant	2005-2012	1 in 6 or 1 in 3 day sampling; 24-hour	TSP	0.02-25.0
East Liverpool	Water Plant	2011	1 in 6 or 1 in 3 day sampling; 24-hour	PM10	0.01-1.50
East Liverpool	Water Plant	2011	1 in 6 or 1 in 3 day sampling; 24-hour	PM2.5	0.002-0.11
East Liverpool	Port Authority	1999-2001; 2003-2012	1 in 6 days; averaged monthly	TSP	0.02-1.90
East Liverpool	Port Authority	2011	1 in 6 days; 24-hour	TSP	0.02-0.89
East Liverpool	Maryland Ave	2003-2012	1 in 6 days; averaged monthly	TSP	0.01-1.0
East Liverpool	Maryland Ave	2011	1 in 6 days; 24-	TSP	0.02-0.63

			hour		

Table 2. Modeling Parameters for Marietta and East Liverpool

Parameter	Marietta	Data Range	East Liverpool	Data Range
Surface meteorology	Mid-Ohio Valley Regional Airport Parkersburg, WV	1991-1995	Pittsburgh International Airport; Pittsburgh, PA	2006-2010
Upper air meteorology	Wright-Patterson Air Force Base Dayton, OH	1991-1995	Pittsburgh International Airport; Pittsburgh, PA	2006-2010
Source of emissions inputs	Process-specific; detailed data provided by facility to U.S. EPA	2001	N/A; generic rate of 1 g/s-m2 over the surface of the site	N/A
Model output data range	1 year average		5 year average	

Table 3. Air-Mn Summary Statistics for Marietta Monitoring Sites (Nov. 2000-Dec. 2011), µg/m^3

Monitoring Site	Eveready* (24-hr)	BKR* (monthly avg)	WCCC* (monthly avg)	Harmar* (monthly avg)	Boaz* (monthly avg)	Neale* (monthly avg)
Distance to source facility	On property	1.6 km	7.2 km	6.4 km	1.6 km	7.2 km
# of observations	8	25	132	55	12	12
Arithmetic Mean	1.13	0.39	0.15	0.10	0.15	0.15
Standard Deviation	0.45	0.31	0.22	0.06	0.07	0.08
Geometric Mean	1.04	0.28	0.09	0.08	0.13	0.14
Lower 95% CI	0.75	0.26	0.11	0.08	0.10	0.11
Upper 95% CI	1.51	0.51	0.19	0.11	0.20	0.21
25th Percentile	0.75	0.16	0.05	0.05	0.10	0.09
50th Percentile	1.15	0.31	0.10	0.08	0.12	0.18
75th Percentile	0.75	0.53	0.17	0.12	0.24	0.21
Minimum observation	0.46	0.05	0.01	0.02	0.05	0.04
Maximum observation	1.90	1.30	1.50	0.38	0.27	0.33
% observations > ATSDR cMRL (0.04 µg/m^3)	100.0	100.0	77.3	78.2	100.0	91.7
% observations > U.S. EPA RfC (0.05 µg/m^3)	100.0	96.0	72.0	72.7	100.0	83.3

** Eveready* = the Eveready Battery Site (OH); *BKR* = the Blue Knob Road Site (OH);
WCCC = Washington County Career Center Site (OH); *Harmar* = Harmar Village Site (OH);
Boaz = Boaz Wastewater Treatment Facility Site (WV); *Neale* = Neale Elementary School Site (WV)

Table 4. Air-Mn Summary Statistics for East Liverpool Monitoring Sites (Mar. 2000-Dec. 2011), µg/m^3

Monitoring Site	Water Plant (24 hr avg)	Water Plant (monthly avg)	Port Authority (monthly avg)	Maryland Ave (monthly avg)
Distance to source facility	0.08 km	0.08 km	2 km	2.1 km
# of observations	525	125	124	112
Arithmetic Mean	1.71	1.55	0.32	0.20
Standard Deviation	2.98	1.24	0.33	0.18
Geometric Mean	0.62	1.10	0.21	0.14
Lower 95% CI	1.46	1.33	0.26	0.16
Upper 95% CI	1.97	1.77	0.38	0.23
25th Percentile	0.19	0.70	0.12	0.07
50th Percentile	0.61	1.30	0.21	0.14
75th Percentile	1.80	2.00	0.41	0.26
Minimum observation	0.02	0.10	0.02	0.01
Maximum observation	25.00	6.80	1.90	1.00
% observations > ATSDR cMRL (0.04 µg/m^3)	97.7	100.0	95.2	92.9

% observations > U.S. EPA RfC (0.05 µg/m³)	96.8	100.0	93.5	86.6

Table 5. Evaluation of discrete vs. composite data for calculating an annual average of measured data to determine annual average adjustment factor In East Liverpool, Ohio (2005-2011)

Water Plant: Annual averages by year discrete and composite data (µg/m³)			discrete/composite
Year	**Discrete data-Arithmetic avg**	**Composite data-Arithmetic avg**	**% difference**
2005	2.56	1.97	23.16
2006	2.97	2.22	25.40
2007	2.35	1.88	19.91
2008	1.71	1.45	14.98
2009	0.82	0.90	-9.45
2010	1.66	1.58	4.60
2011	0.99	0.92	7.36
2005-2011 Average	**1.87**	**1.56**	**16.42**

Table 6. Modeled estimates of TSP air-Mn (µg/m³) compared to measured outdoor TSP air-Mn data (TSP air-Mn in µg/m³) in Marietta, Ohio and East Liverpool, Ohio (2000-2011)

	Modeled Marietta TSP Annual Avg	**Measured Marietta Range: TSP Annual Avg***	**Modeled East Liverpool TSP Annual Avg**	**Measured East Liverpool Range: TSP Annual Avg***
Min	0.04	0.01-0.05	0.004	0.01-0.10
Max	0.96	0.27-1.50	1.93	1.0-6.80
25th Percentile	0.13	0.05-0.16	0.06	0.07-0.70
50th Percentile	0.16	0.08-0.31	0.09	0.14-1.30
75th Percentile	0.19	0.12-0.53	0.32	0.26-2.0
Geometric mean	0.16	0.08-0.28	0.11	0.14-1.10
Arithmetic mean	0.18	0.18-0.39	0.27	0.20-1.55

**Average over all air sampling sites*

Table 7. Exposure Matrices: Annual Estimates of TSP, PM_{10}, and $PM_{2.5}$ air-Mn (µg/m³) in Marietta and East Liverpool (2000-2011)

	Estimated East Liverpool TSP Ann Avg	**Estimated Marietta TSP Ann Avg**	**Estimated East Liverpool PM_{10} Ann Avg**	**Estimated Marietta PM_{10} Ann Avg**	**Estimated East Liverpool $PM_{2.5}$ Ann Avg**	**Estimated Marietta $PM_{2.5}$ Ann Avg**
Min	0.0042	0.0400	0.0015	0.0332	0.0002	0.0084
Max	1.9337	0.9600	0.6768	0.7968	0.0715	0.2016
25th Percentile	0.0599	0.1300	0.0210	0.1079	0.0022	0.0273
50th Percentile	0.0940	0.1600	0.0329	0.1328	0.0035	0.0336
75th Percentile	0.3203	0.1900	0.1121	0.1577	0.0119	0.0399
90th Percentile	0.8728	0.2410	0.3055	0.2000	0.0323	0.0506
95th Percentile	1.0290	0.5100	0.3602	0.4233	0.0381	0.1071
99th Percentile	1.4798	0.7521	0.5179	0.6242	0.0548	0.1579
Geometric mean	0.1073	0.1608	0.0376	0.1335	0.0040	0.0338
Arithmetic mean	0.2687	0.1845	0.0941	0.1531	0.0099	0.0387